Stacking fault energy in some single crystals

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Abstract: The stacking fault energy of single crystals has been reported using the peak shift method. Presently studied all single crystals are grown by using a direct vapor transport (DVT) technique in the laboratory. The structural characterizations of these crystals are made by XRD. Considerable variations are shown in deformation (α) and growth (β) probabilities in single crystals due to off-stoichiometry, which possesses the stacking fault in the single crystal.

Key words: single crystals; X-ray diffrectograms; deformation probability; growth probability; stacking fault

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1. Introduction

A basic understanding of the deformation characteristics and mechanical behavior of materials requires the knowledge of the stacking-fault energy (SFE). This aspect is relevant because various mechanical properties such as strength, toughness and fracture are severely affected by stacking-fault energy (SFE) due to its direct influence on the slip mode, deformation twinning and martensitic transformations. Thus, in alloy design, it is important to understand how stacking-fault energy (SFE) is affected by composition. Lamellar solids of transition metal dichalcogenides (TMDC)MX_2 (M = Mo, W, Nb, Ta and X = S, Se, Te) have been extensively studied because of their excellent lubricating properties and photovoltaic behavior. These materials, being semiconducting and of a layered structure, may undergo structural and electronic transitions under pressure. They typically have a hexagonal structure, which is composed of two-dimensional sheets stacked on top of one another. Each sheet is tri-layered with a metal atom in the middle that is covalently bonded to chalcogen atoms in the top and bottom layers. The covalently bonded sheets are held together by weak van der Waals forces, which permit them to shear easily. At high pressures the fluid lubricants squeeze out from in-contact surfaces, causing high friction and wear. With lamellar solids such as TMDCs, shearing takes place more easily when loads are high. Hence, lamellar solids are well-suited to extreme pressure lubrication. Structural transitions and metallization are of relevance in its application as lubricant. These crystals become superconducting when intercalated with alkali and alkaline earth metals[1−19]. The study of stacking faults is very important one, because it plays an important role in the description of defects. The conversion behaviour of a solar cell is closely related to the perfection of the electrode material and since stacking faults play a fundamental role in the description of structural defects, their study is of both practical and theoretical interest. The enhanced conduction of the stacking fault along the c-axis is difficult to understand because of the extreme 2D characters of the layered compounds of $MoSe_2$. The only way to understand this conduction is by supposing the presence of stacking faults in these crystals. We have reported some structural, electric and optical properties of TMDC materials[1−15] briefly. Very recently, Sumesh *et al.*[16, 17] have reported specific contact resistance at In-n$MoSe_2$ interfaces and current–voltage–temperature characteristics experimentally. The stacking fault energy of various compounds has been studied by various researchers[18−31]. It is clear from the literature survey that research on the stacking fault energy of the various intercalated and doping compounds of $MoSe_2$ is almost negligible. Hence, in the present article, we have decided to work on intercalated In_xMoSe_2 ($0 \leqslant x \leqslant 1$) and doped $MoRe_{0.005}Se_{1.995}$, $MoRe_{0.001}Se_{1.999}$ and $Mo_{0.995}Re_{0.005}Se_2$ single crystals.

2. Experimental methodology

All of the studied single crystals were grown by using the direct vapor transport (DVT) method inside a dual zone horizontal furnace[1−15]. In the present case, a furnace controlled by a micro controller with thermal profile programming facilities and a solid state relay (SSR) based power unit for the two zones of the furnace with suitable back up to take care of power supply breakups has been used. A high quality fused quartz tube is used for crystal growth.

The formation and occurrence of crystal imperfections known as stacking faults is important to the mechanisms and models postulated to explain work hardening and recovery of closely packed metals and alloys. Stacking faults represent disorders in stacking atomic planes which are formed during the process of crystal growth, plastic deformation, phase transformations and by the condensation and collapse of vacancy discs. In a face centered cubic (FCC) structure, the stacking fault is a thin slab with a hexagonal closely packed (HCP) structure and in HCP materials the stacking fault is a thin layer with an FCC structure. The faults are formed when disorders in stacking the closely packed layers occur. The TMDC compounds have the general formula TX_2, where T is a transition metal from IV-B, V-B and the VI-B group of the periodic table and

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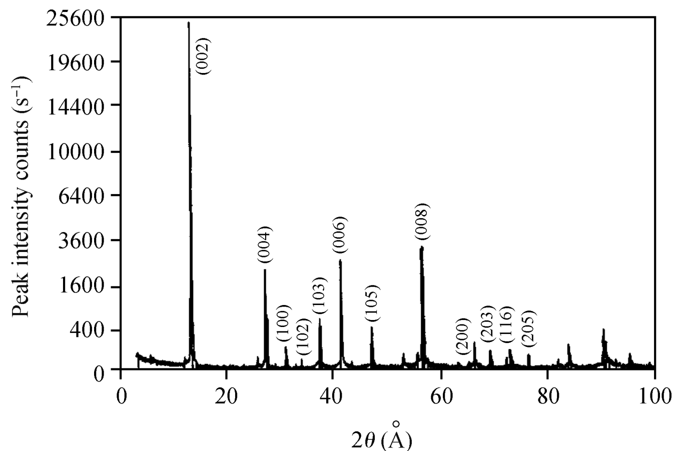

Fig. 1. X-ray diffractograms of $In_{0.25}MoSe_2$.

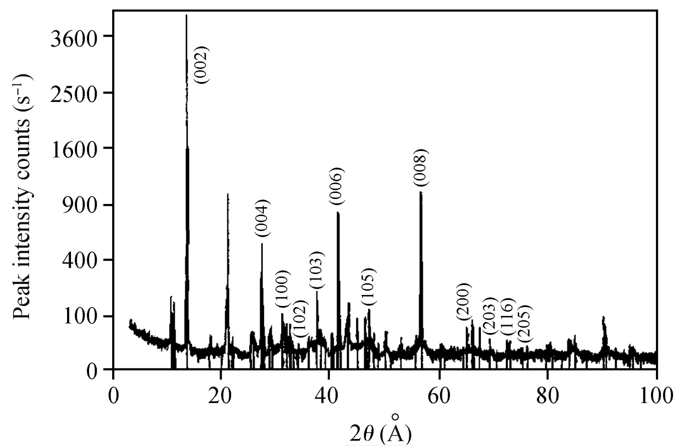

Fig. 4. X-ray diffractograms of $InMoSe_2$.

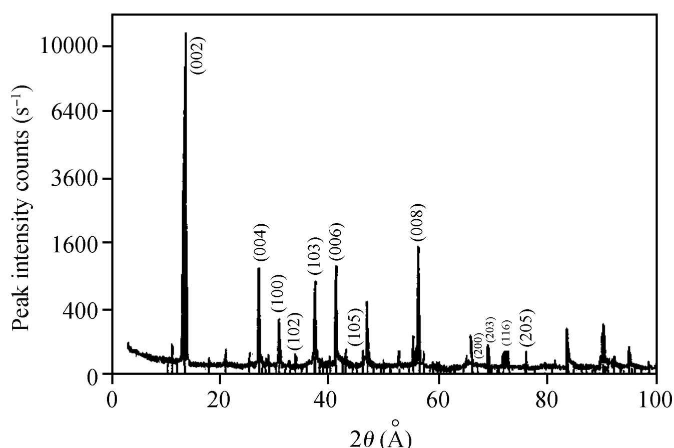

Fig. 2. X-ray diffractograms of $In_{0.50}MoSe_2$.

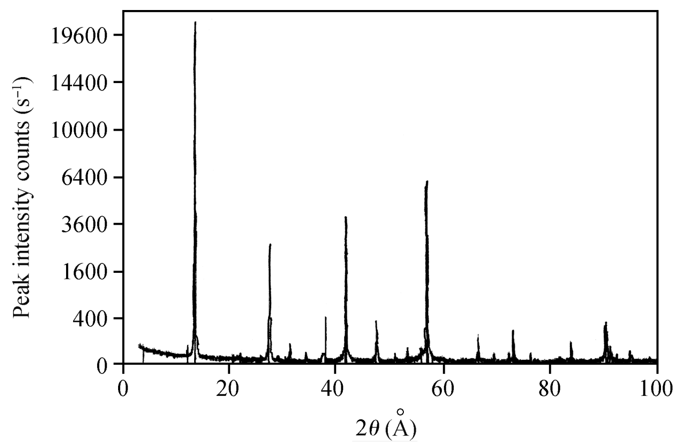

Fig. 5. X-ray diffractograms of $MoRe_{0.005}Se_{1.995}$ single crystal.

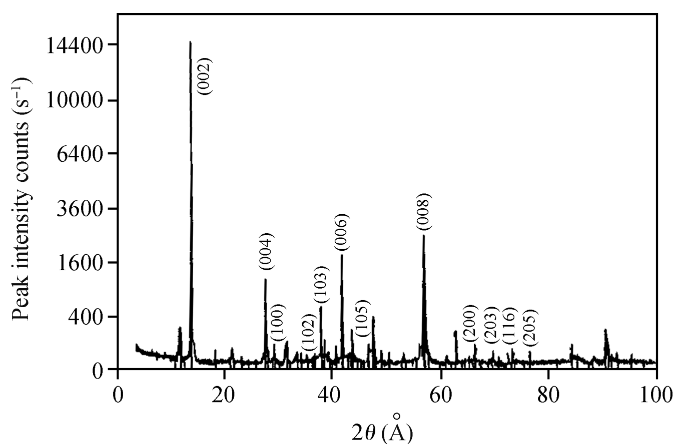

Fig. 3. X-ray diffractograms of $In_{0.75}MoSe_2$.

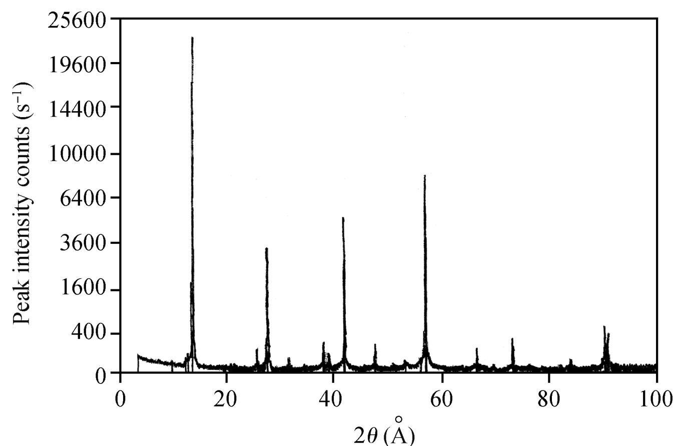

Fig. 6. X-ray diffractograms of $MoRe_{0.001}Se_{1.999}$ single crystal.

X is one of the chalcogens sulfur, selenium or tellurium. The basic structure of loosely coupled X–T–X sheets makes such materials extremely interesting such that, within a layer, the bonds are strong, while between the layers they are remarkably weak. Basically, the stacking faults in the single crystals are detected by using X-rays. With a view to examining the proposed correlation between stacking faults and the deformation-induced structural transformation, the stacking fault probability in presently taken single crystals has been determined by X-ray diffraction methods. In the present study all of the single crystals are found to be HCP type in nature.

The X-ray diffractogram was recorded using a Philips X-ray diffractometer using CuKα radiation. For this purpose, many small crystals from each group were finely ground using an agate mortar and filtered through a 106-μm sieve to obtain grains of nearly equal size. The X-ray diffractograms of

Table 1. Structural parameters used in the calculation of stacking fault energy for Re-doped single crystals.

hkl value	$MoRe_{0.005}Se_{1.995}$			$MoRe_{0.001}Se_{1.999}$			$Mo_{0.995}Re_{0.005}Se_2$		
	d-value (Å)	Peak intensity count ($\beta_{2\theta}$) (s^{-1})	Angle (2θ) (Å)	d-value (Å)	Peak intensity count ($\beta_{2\theta}$) (s^{-1})	Angle (2θ) (Å)	d-value (Å)	Peak intensity count ($\beta_{2\theta}$) (s^{-1})	Angle (2θ) (Å)
102	2.6158	0.080	34.255	2.6111	0.140	34.315	2.6082	0.080	34.395
103	2.3774	0.060	37.810	2.3756	0.080	37.840	2.3756	0.120	37.840
105	1.9152	0.100	47.430	1.9112	0.080	47.535	1.9147	0.080	47.445

Table 2. Structural parameters used in the calculation of stacking fault energy for In_xMoSe_2 ($0 \leqslant x \leqslant 1$) single crystals.

hkl value	$In_{0.25}MoSe_2$			$In_{0.50}MoSe_2$			$In_{0.75}MoSe_2$			$InMoSe_2$		
	d-value (Å)	Peak intensity count ($\beta_{2\theta}$) (s^{-1})	Angle (2θ) (Å)	d-value (Å)	Peak intensity count ($\beta_{2\theta}$) (s^{-1})	Angle (2θ) (Å)	d-value (Å)	Peak intensity count ($\beta_{2\theta}$) (s^{-1})	Angle (2θ) (Å)	d-value (Å)	Peak intensity count ($\beta_{2\theta}$) (s^{-1})	Angle (2θ) (Å)
102	2.6158	0.080	34.255	2.6111	0.140	34.315	2.6082	0.080	34.395	2.6097	0.240	34.335
103	2.3774	0.060	37.810	2.3756	0.080	37.840	2.3756	0.120	37.840	2.3774	0.080	37.810
105	1.9152	0.100	47.430	1.9112	0.080	47.535	1.9147	0.080	47.445	1.9171	0.080	47.380

Table 3. Stacking fault probabilities of In_xMoSe_2 ($0 \leqslant x \leqslant 1$) single crystals.

Stacking fault probability	$In_{0.25}MoSe_2$	$In_{0.50}MoSe_2$	$In_{0.75}MoSe_2$	$InMoSe_2$
α	0.0025037	0.0026711	0.0023574	0.0033694
β	0.0025299	0.0027837	0.0022524	0.0032857

Table 4. Stacking fault probabilities of Re-doped $MoSe_2$ single crystals.

Stacking fault probability	$MoRe_{0.005}Se_{1.995}$	$MoRe_{0.001}Se_{1.999}$	$Mo_{0.995}Re_{0.005}Se_2$
α	0.0025037	0.0026711	0.0023574
β	0.0024799	0.0026637	0.0023324

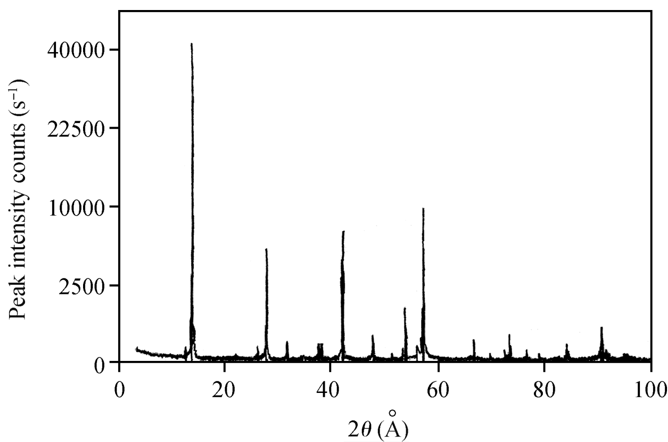

Fig. 7. X-ray diffractograms of $Mo_{0.995}Re_{0.005}Se_2$ single crystal.

all the single crystals are displayed in Fig. 1–7. The structural parameters used in the calculation of the stacking fault energy (SFE) taken from the X-ray diffractograms of the single crystals are tabulated in Tables 1 and 2, which are used in present calculation.

The stacking fault probabilities of the samples were measured by using peak shift methods. According to Warren's X-ray diffraction theory[18], the diffraction peak shift is due to the deformation fault in the HCP crystal. Hence, such probability can be determined by measuring the peak shift. For that, the formulas of deformation and growth probabilities given by Warren[18] are as follows

$$B_{2\theta} = \frac{360 \tan\theta}{\pi^2} l \left(\frac{d}{c}\right)^2 (3\alpha + 3\beta), \quad l \text{ even}, \tag{1}$$

and

$$B_{2\theta} = \frac{360 \tan\theta}{\pi^2} l \left(\frac{d}{c}\right)^2 (3\alpha + \beta), \quad l \text{ odd}, \tag{2}$$

where $B_{2\theta}$ denotes the full width at half the maximum intensity, d is the hkl spacing, c is equal to $2d_{002}$, and α and β are the deformation fault probability and the growth probability. Values of the deformation fault probability α and the growth probability β have been estimated from the observed peak shifts and the peak asymmetry, respectively. The presently calculated values of α and β are shown in Tables 3 and 4. All the calculations are performed for (102), (103) and (105) reflections. The peak displacement due to faults in the HCP structure

is usually very small and therefore, it is in general advisable to try measuring a pair of close reflections.

3. Results and discussion

From studies of Tables 3 and 4, it is seen that there is a significant variation shown in the deformation fault probability (α) and growth probability (β) due to off-stoichiometry i.e. composition of indium in the $MoSe_2$ and Re-doped $MoSe_2$ viz. $MoRe_{0.005}Se_{1.995}$, $MoRe_{0.001}Se_{1.999}$ and $Mo_{0.995}Re_{0.005}Se_2$ single crystals. The variation of stacking fault i.e. both probabilities is due to the creation of the defects in the crystal. The values of α and β are seen nearly of the same order. Any theoretical or experimental proof of such types of calculation is not available in the literature so it is difficult to compare our results with them and make any strong remarks. The calculation of the stacking fault may be considered as one of the guidelines for further detailed study of defects and various properties of crystals.

It was shown by Cockyne *et al.*[19] that significant improvement in resolution of the structure of lattice defects could be obtained from dark field electron micrographs taken in weakly diffracted beams. Ray and Cockyne[20] have used the weak beam technique for directly observing the splitting of dislocations into partials of Si. Since then, several investigators[21−25], most recently Mao and Knowles[26], have observed the dissociation of lattice dislocations into partials. The presence of stacking faults has been studied by Agarwal *et al.*[27, 28] in WS_2. $WS_{1.8}$ and WSe_2 single crystals. All these investigators have used the spacing between partials to estimate the stacking fault energy (SFE) in the crystal compounds. Gross and Teichler[29] have formulated a real space method, Kenway[30] has adopted an atomic lattice stimulation and Xiliang *et al.*[31] have used a method based on an improved embedded-atom method for theoretical estimation of stacking fault energies in different materials. All these estimations when compared with stacking fault energy measurements made using weak beam techniques show a favourable agreement.

The low values of stacking fault probabilities allows for easy gliding on the basal plane of In_xMoSe_2 ($0 \leqslant x \leqslant 1$) and Re-doped $MoSe_2$ viz. $MoRe_{0.005}Se_{1.995}$, $MoRe_{0.001}Se_{1.999}$ and $Mo_{0.995}Re_{0.005}Se_2$ layers thus leading to easy creation of stacking faults and its excellent properties as solid lubricating agent. The above results indicate that the peak-shift method described in the present work has been successfully developed for the determination of deformation fault probability (α) and growth probability (β).

4. Conclusion

X-ray diffractogrms have clearly shown that the difference in the presently studied single crystals is due to off-stoichiometry. The analysis of the deformation fault probability (α) and growth probability (β) of all the single crystals has shown that indium intercalation and Re-doping affect the stacking fault probabilities. The experimental proof is not available in the literature, but the present investigation provides an important set of data for most of the single crystals, which can be very useful for further comparison either with theory or experiment. A study on the stacking fault of other single crystals is in progress.

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